

Using Wet Air Oxidation Technology to Destroy Tetraphenylborate in SRS Tank 48H



SRNLTM
SAVANNAH RIVER NATIONAL LABORATORY

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Outline

- **Background**
- **Applications**
- **Technology development plan**
- **Test objectives**
- **Scope of work**
- **Test results**
- **Summary/Path forward**

Background

- Tank 48H in Savannah River Site (SRS) contains tetraphenylborate (TPB) from the operation of an In-Tank Precipitation (ITP) process
- ITP process used NaTBP to precipitate CsTPB
- TPB is not compatible with SRS waste treatment program
 - Needs to be removed or destroyed before the tank can be returned to Tank Farm service
- Tank 48H contains ~250,000 gallons of alkaline slurry
 - Concentration of KTPB and CsTPB = ~21 g/L

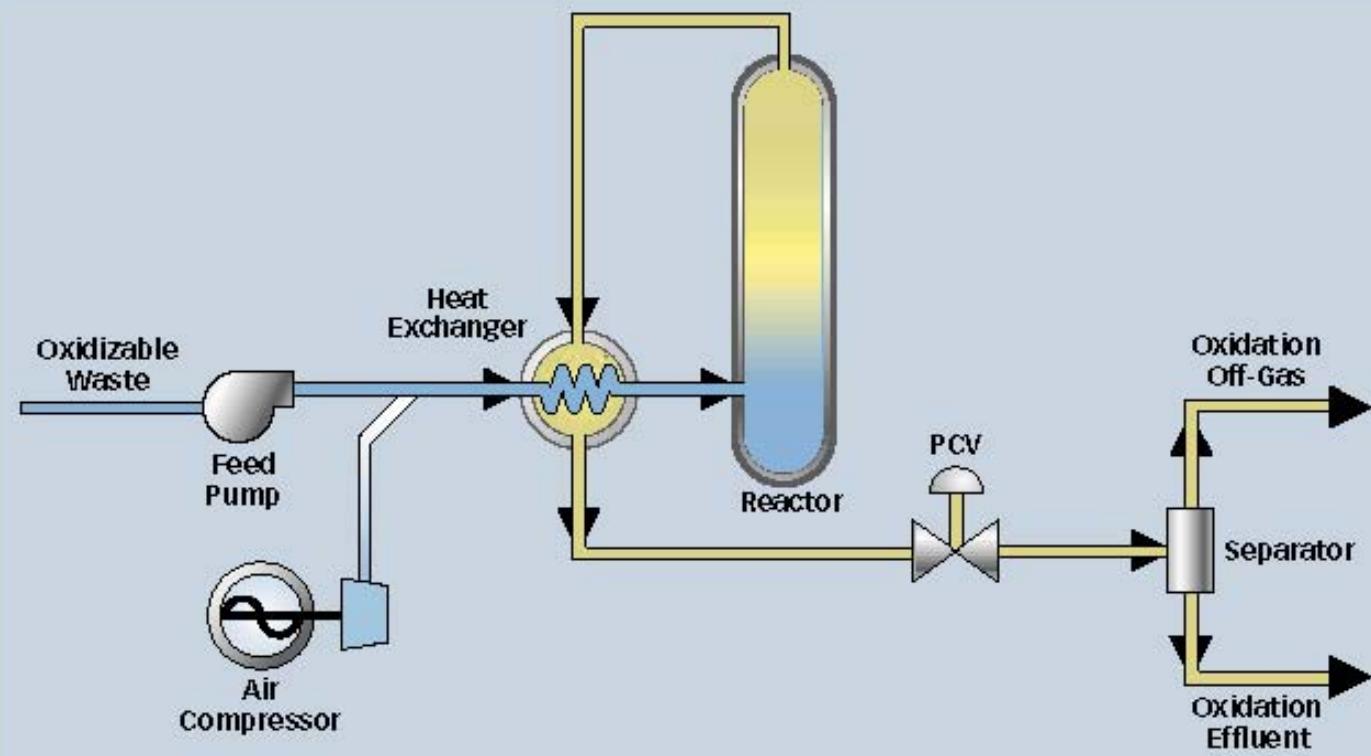
Wet Air Oxidation (WAO) Background

- Aqueous phase process in which organic and inorganic components are oxidized using air (O_2)
- Reaction products
 - CO_2 , H_2O , SO_4 , HCl , and low molecular weight short chain oxygenated organics (carboxylic acids), e.g., acetic acid
- Typical operating ranges
 - Temperature: 100 - 320°C (sub-critical)
 - Pressures: 7 - 210 atmospheres (sub-critical)
 - Reaction times: 15 - 120 minutes
 - Feed flow rate: 1 - 220 gpm per unit
 - Chemical oxygen demand (COD): 10,000 - 150,000 mg/L
 - Total organic carbon (TOC) equivalent of approximately 5,000 - 75,000 mg/L

WAO is a EPA Best Demonstrated Available Technology (BDAT) for a variety of P & U listed organics.

WAO Process Schematic

Typical WAO flow diagram



Zimpro® WAO Skid on a Truck



Typical WAO Reactions

➤ Overall reactions

- Organics + O₂ → CO₂ + H₂O + RCOOH*
- Organic Cl + O₂ → Cl⁻¹ + CO₂ + RCOOH*
- Organic N + O₂ → NH₃ + CO₂ + RCOOH*
- Sulfur species + O₂ → SO₄⁻²
- Phosphorus species + O₂ → PO₄⁻³
- Organic B + O₂ → BO₂⁻¹ + CO₂ + RCOOH*

- *short chain organic acids such as acetic acid make up the major fraction of residual organic compounds

Advantages of WAO

- Proven technology - WAO successfully commercialized for 50+ years.
 - > 200 full-scale systems have been constructed and operated
 - 130 sewage sludge
 - 90 petrochemical, chemical, and pharmaceutical wastes
 - 25 ethylene plant spent caustic
 - Experienced vendor available
- Continuous process with fairly short reaction times
- Relatively small process footprints
- Generally requires no use of chemicals
- No increase in waste volume (unless the waste has to be diluted)
- High thermal efficiency – essentially an autothermal operation
- Corrosion-resistant materials available
- Highly automated operation
- Robust
- Off-gas has negligible NO_x, SO_x, and particulates

WAO APPLICATIONS

- Spent caustic from petroleum refineries and ethylene plants
- Municipal sewage sludge
- Wet air regeneration
- Organic wastes in pharmaceutical and chemical industries
- Acrylonitrile
- Paper manufacturing waste – filler clays, sludge, pulping liquor
- Metallurgical coking
- Polysulfide rubber
- Textile sludge
- Tannery waste
- Monosodium glutamate
- Industrial sludges
- Explosives

- Petroleum Refinery Spent Caustic WAO Unit (3 gpm flow rate) - Rio de Janeiro, Brazil



Zimpro® WAO System

DoD WAO APPLICATION

- DoD 27-gpm WAO unit at Texas Molecular site in Deer Park, Texas
- Start-up was January 2007



WAO is being used to destroy neutralized chemical warfare materiel – mustard agents, nerve agents, and other binary weapon components

WAO Radioactive Applications

- Bench-scale WAO was successfully applied in the 1990s to destroy organics (EDTA, HEDTA) in Hanford Site radioactive waste.
 - Organics destruction based on TOC for both simulant and radioactive waste was > 98%.
- Ontario Hydro (in Canada) used a 12 gpm commercial-scale WAO unit in the 1990s to treat EDTA waste contaminated with low levels of radionuclides.
 - EDTA destruction was > 99.5%.

Potential DOE Complex-Wide WAO Applications

- Destruction of organics in general
 - Residual oxalic acid used to dissolve sludges
- Sludge Mass Reduction Program
 - Faster dissolution rates of aluminum in sludges

WAO Technology Development Plan

- **Bench-scale simulant testing – Completed**
 - Batch autoclave experiments
 - Demonstrate destruction of TPB (< 2 mg/L)
- **Continuous-flow pilot-scale simulant testing – TBD**
 - Optimize bench-scale process conditions
 - Determine off-gas composition
 - Demonstrate stable and safe steady-state operations
 - Extended MOC testing
- **Bench-scale radioactive testing – TBD**
 - Confirm destruction efficiencies and rates
- **Integrated continuous-flow pilot-scale simulant testing – TBD**
 - Includes HEPA filters, off-gas treatment system if needed, blowers, etc.

WAO Bench-Scale Testing Objectives

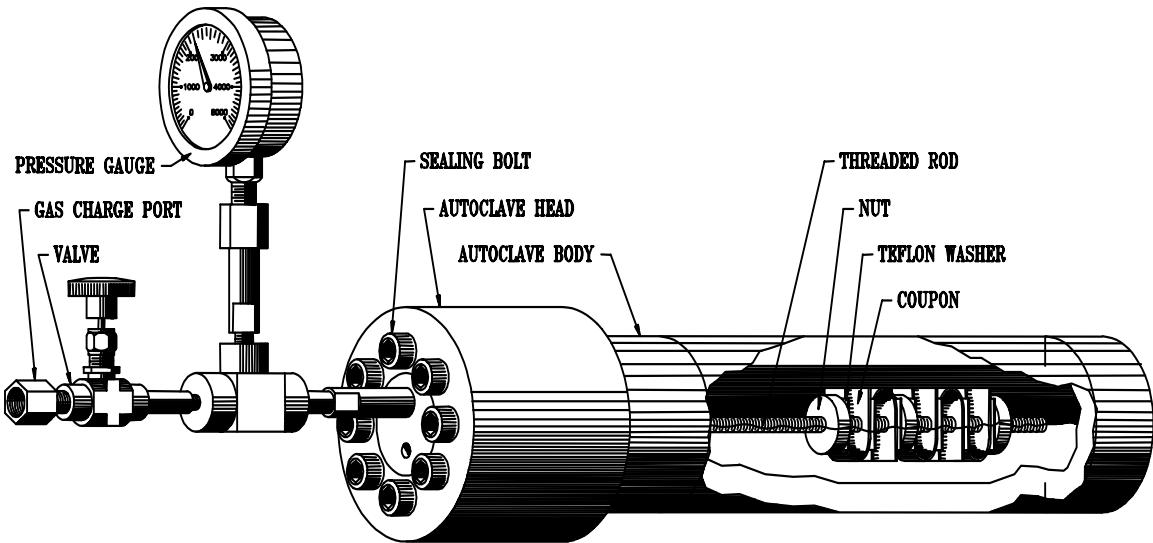
- Determine optimum conditions to destroy TPB
 - Temperature, pressure, reaction time, air/oxygen requirements, catalysts, and feed dilution
 - Targets
 - TPB: < 2 mg/L
 - Triphenylborane (3PB): < 10 mg/L
 - Diphenylborinic acid (2PB) : < 10 mg/L
 - Phenylboronic acid (1PB) : < 10 mg/L
- Identification of the materials-of-construction (MOC)
- Quantify secondary byproducts
- Provide data for preliminary full-scale system design parameters
 - Including evaluation of process economics

WAO Bench-Scale Testing Scope of Work

- Ten Screening Tests (Phase 1)
- Four Optimization Tests (Phase 2)
- Quadruplicate Confirmation Tests (Phase 3)
- One 100-hour MOC Test at confirmation test conditions

Bench-Scale Shaking Autoclave with MOC Coupons

SHAKING AUTOCLAVE



Zimpro® WAO System

Using Wet Air Oxidation Technology to Destroy
Tetraphenylborate in SRS Tank 48H: WSRC-STI-2007-00518

Treated Waste & Off-Gas Analysis

➤ Treated Waste

- TPB, 3PB, 2PB, 1PB, phenol, biphenyl
- Semi-volatile/volatile organic compounds (SVOC/VOC) e.g., benzene
- Organic acids
- Metals and inorganic anions

➤ Off-Gas

- O₂, N₂, CO₂, CO, H₂
- Total hydrocarbons (THC)
- Volume of off-gas generated
- SVOC/VOC e.g., benzene

Test Conditions

➤ Investigated the effect of the following variables

- Temperature
- Time
- Dilution with water
- Dilution with caustic and its concentration
- Catalyst and its concentration
- Antifoam
- Baffled and non-baffled autoclave

Screening Test Conditions

	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 9	Test 10	Test 11
Temp. (°C)	300	300	240	300	200	280	280	300	300	300
Time (hr.)	1	3	3	3	3	3	1	3	4	3
Baffles	No	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Antifoam-IIT B52 (ppmv)	No	2000	2000	2000	2000	No	No	No	2000	2000
Cu Catalyst (mg/L)	No	No	No	500	500	500	500	1000	500	750
Feed Slurry Dilution	1:1 (water)	1:1 (water)	1:1 (water)	1:1 (2M NaOH)	1:1 (2M NaOH)	1:1 (4M NaOH)	1:1 (4M NaOH)	1:1 (4M NaOH)	1:1 (2M NaOH)	1:1 (2M NaOH)

Autoclave material – Nickel 200

Autoclave volume – 500 mL

Feed volume – 100 mL

Cu catalyst – CuSO₄.5H₂O solution

Operating pressure = 75 - 163 atmospheres. **Note:** Operating pressure for a continuous-flow system is typically about 5 to 50% lower.

Test 8 was discarded because of leakage during testing.

Optimization Test Conditions

	Test 12	Test 13	Test 14	Test 15
Temp. (°C)	280	300	280	300
Time (hr.)	3	3	3	3
Baffles	Yes	Yes	Yes	Yes
Antifoam-IIT B52 (ppmv)	2000	2000	2000	2000
Cu Catalyst (mg/L)	500	500	500	500
Feed Slurry Dilution	1:1 (2M NaOH)	1:1 (2M NaOH)	1:2 (2M NaOH)	1:2 (2M NaOH)

Autoclave material – Nickel 200

Autoclave volume – 500 mL

Feed volume – 100 mL

Cu catalyst – CuSO₄.5H₂O solution

Operating pressure = 145 - 163 atmospheres. Note: Operating pressure for a continuous-flow system is typically about 5 to 50% lower.

Screening Tests – Pictures of Treated Simulants

Test #	Conditions	Treated Simulant	Conclusion
Test 2	300°C, 3 hours, baffled, antifoam, no copper , 1:1 dilution with water		Residual biphenyl; Catalyst needed
Test 4	300°C, 3 hours, baffled, antifoam, 500 mg/L copper , 1:1 dilution with 2M NaOH		Trace biphenyl; More catalyst or more time needed

Screening Tests – Pictures of Treated Simulants

Test #	Conditions	Treated Simulant	Conclusion
Test 6	280°C, 3 hours, baffled, no antifoam, 500 mg/L copper, 1:1 dilution with 4M NaOH		Residual biphenyl; Increased caustic insufficient
Test 7	280°C, 1 hour, baffled, no antifoam, 500 mg/L copper, 1:1 dilution with 4M NaOH		Residual biphenyl; Increased caustic insufficient

Optimization Tests – Pictures of Treated Simulants

Test #	Conditions	Treated Simulant	Conclusion
Test 13	300°C, 3 hour, baffled, antifoam, 500 mg/L copper, 1:1 dilution with 2M NaOH. Same conditions as Test 4.		Residual biphenyl; <u>Note:</u> Achieving reproducibility has been difficult.
Test 15	300°C, 3 hours, baffled, antifoam, 500 mg/L copper, 1:2 dilution with 2M NaOH		Residual biphenyl but generally less than those for 1:1 dilution

Screening Tests – Treated Simulant Data

	Units	Undiluted Feed	Test 1*	Test 2	Test 3*	Test 4	Test 5*	Test 6	Test 7	Test 9	Test 10	Test 11
TPB	mg/L	17,980	---	<0.8	---	<0.8	---	<1.0	<0.8	<1.0	2	3
3PB	mg/L	<10	---	<10	---	<10	---	<10	<10	<10	<10	<10
2PB	mg/L	<10	---	<10	---	<10	---	<10	<10	<10	<10	<10
1PB	mg/L	<10	---	<10	---	<10	---	<10	<10	<10	<10	<10
Phenol	mg/L	958	---	<10	---	<10	---	<10	<10	<10	<10	<10
Soluble Biphenyl**	mg/L	---	---	<10	---	<10	---	<10	<10	<10	<10	<10
Floating Biphenyl	mg/L	560	---	85	---	<10	---	503	1,190	61	43	176
pH	---	---	12.0	9.4	12.6	12.8	12.9	14.5	14.1	14.4	14.3	14.4

* Treated slurry simulants from tests 1, 3, and 5 were not analyzed.

** Soluble biphenyl is biphenyl dissolved in the aqueous phase.

Test 8 was discarded because of leakage during testing.

TPB destruction > 99.97%. TPB daughter compounds (3PB, 2PB, 1PB), and phenol are destroyed to below detection limits.

Optimization Tests – Treated Simulant Data

	Units	Undiluted Feed	Test 12	Test 13	Test 14	Test 15
TPB	mg/L	17,980	<0.8	<0.8	0.8	1
3PB	mg/L	<10	<10	<10	<10	<10
2PB	mg/L	<10	<10	<10	<10	<10
1PB	mg/L	<10	<10	<10	<10	<10
Phenol	mg/L	958	<10	<10	<10	<10
Soluble Biphenyl*	mg/L	---	<10	<10	<10	<10
Floating Biphenyl	mg/L	560	91*	8*	14*	<10*
pH	---	---	14.3	13.3	14.4	14.2

* Soluble biphenyl is biphenyl dissolved in the aqueous phase.

TPB destruction > 99.99%. TPB daughter compounds (3PB, 2PB, 1PB), and phenol are destroyed to below detection limits.

Screening Tests – Off-Gas Data

	Units	Test 1	Test 2	Test 3	Test 4	Test 5	Test 6	Test 7	Test 9	Test 10	Test 11
Off-Gas Volume	L	13.3	11.0	11.4	10.2	12.0	11.1	14.0	12.2	13.1	10.3
Off-Gas Temp.	°C	19.3	18.9	19.3	18.3	18.6	18.5	19.8	18.3	20.0	18.3
CO ₂	vol%	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5	<0.5
O ₂	vol%	14.4	7.1	12.7	2.9	11.4	7.1	10.8	7.3	8.3	5.3
N ₂	vol%	82.9	89.7	84.3	96.1	86.7	93.2	90.4	92.1	89.8	92.9
CO	vol%	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
THC (as ethane - C ₂ H ₆)	ppmv	3,000	3,160	3,390	860	870	1,390	1,170	720	880	1,250
Methane (CH ₄)	ppmv	<50	<50	<50	<50	<50	<50	<50	<50	<50	<50
Hydrogen	vol%	0.054	<0.05	0.052	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
O ₂ Uptake	g/L*	17.8	31.5	22.0	38.3	23.2	33.4	26.3	33.8	31.0	37.4

* This is the mass of oxygen consumed by the oxidation of constituents in the slurry. The units are grams of oxygen per liter of slurry treated in the autoclave.

Copper catalyst appears to lower THC

Optimization Tests – Off-Gas Data

	Units	Test 12	Test 13	Test 14	Test 15
Off-Gas Volume	L	11.4	11.9	11.0	14.2
Off-Gas Temp.	°C	17.3	17.9	62	19.3
CO ₂	vol%	<0.5	<0.5	<0.5	<0.5
O ₂	vol%	12.3	11.4	12.4	13.1
N ₂	vol%	89.6	90.5	88.0	87.9
CO	vol%	<0.1	<0.1	<0.1	<0.1
THC (as ethane - C ₂ H ₆)	ppmv	2,250	2,255	2,290	1,370
Methane (CH ₄)	ppmv	<50	<50	<50	<50
Hydrogen	vol%	0.054	<0.05	0.052	<0.05
O ₂ Uptake	g/L*	23.5	25.1	24.2	21.1

* This is the mass of oxygen consumed by the oxidation of constituents in the slurry. The units are grams of oxygen per liter of slurry treated in the autoclave.

Copper catalyst appears to lower THC

General Observations

- WAO destroys TPB (<1 mg/L); 3PB, 2PB, 1PB, & phenol (<10 mg/L)
 - 1 hour at 280 °C with Cu (Test 7) or 3 hours at 300 °C without Cu (Test 2)
 - 1, 3 and 5 gpm units with 75% operational time at 1:1 feed dilution will treat Tank 48H Waste (250,000 gal) in about 15, 5 and 3 months respectively.
- Destruction of biphenyl requires more aggressive conditions
 - Minimum 3+ hours at 300 °C with Cu and antifoam
- High temperatures lead to low residual biphenyl in the treated slurry
- Increasing reaction time results in low residual biphenyl in the treated slurry
- Cu catalyst improves residual biphenyl destruction and lowers THC in the off-gas
- Catalytic effect of Cu diminishes at Cu concentrations \geq 750 mg/L
 - Cu concentrations less than 500 mg/L may be adequate

General Observations

- Diluting the feed slurry with 2M NaOH solution (instead of 4M) leads to adequate slurry pH levels to render Cu catalyst soluble.
- Increasing feed slurry dilution seems to decrease residual biphenyl in the treated slurry
 - Dilutions less than 1:1 may be adequate.
- Antifoam appears to enhances residual biphenyl destruction.
- Flammability of benzene appears potentially resolvable based on the off-gas total hydrocarbon (THC) data
 - Maximum THC value = 0.34% (Test 4 = 0.086%)
 - Benzene LFL = 1.4% @ 25 °C
 - Off-gas data from closed autoclaves may not match flow-through system
 - Continuous-mode testing would give more realistic off-gas data

Floating Biphenyl on Treated Simulant

- Attributed to floating on the aqueous phase and/or present as vapor
- Issues
 - Subliming, clogging demister, valves, and off-gas system
 - Potential resolutions
 - Increase feed dilution factor
 - Reactor designed to improve mixing, e.g., baffles, static mixer, reactor with high aspect ratio, etc.
 - Partial recirculation of treated effluent
 - Decanting and recycling
 - Immersion methods e.g., activated carbon or a surfactant
 - Strip to off-gas and use thermal/catalytic oxidation (TO/CO)
 - Purge biphenyl vapor at reactor outlet to off-gas and use TO/CO
 - Allows lower temperature WAO and shorter residence times

Confirmation Test Conditions

- A review of all the test data indicated Test 13 or 4 conditions were best for the confirmation tests

Test 16	
Temp. (°C)	300
Time (hr.)	3
Baffles	Yes
Antifoam-IIT B52 (ppmv)	2000
Cu Catalyst (mg/L)	500
Feed Slurry Dilution	1:1 (2M NaOH)

Autoclave material – Nickel 200

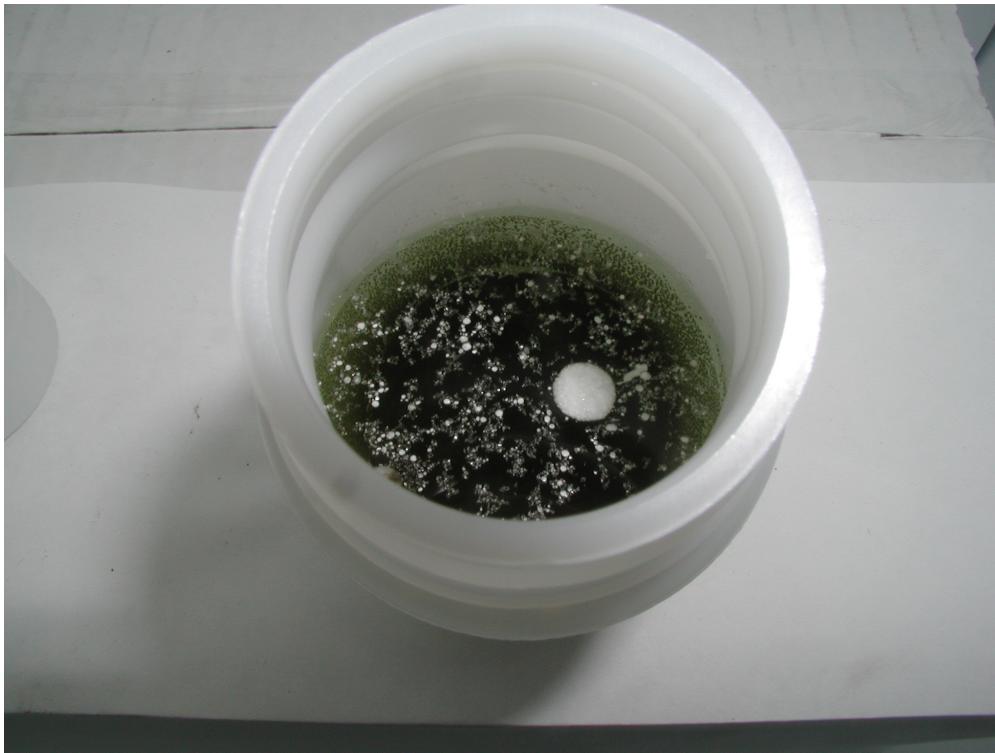
Autoclave volume – 500 mL

Feed volume – 100 mL

Cu catalyst – CuSO₄.5H₂O solution

Confirmation Test (16A) – Picture of Treated Simulant

- Test Condition – 300°C, 3 hours, baffled, antifoam, 500 mg/L copper, 1:1 dilution with 2M NaOH. **Same conditions as Test 4 or 13.**



Confirmation Tests – Treated Simulant Data

	Units	Diluted Feed Slurry Conc. (Calculated)	Test 16A	Test 16B	Test 16C	Test 16D
TPB	mg/L	9,186	<0.8	<1.0	<0.8	<1.0
3PB	mg/L	<5	<10	<10	<10	<10
2PB	mg/L	<5	<10	<10	<10	<10
1PB	mg/L	<5	<10	<10	<10	<10
Phenol	mg/L	476	<10	<10	<10	<10
Soluble Biphenyl ^a	mg/L	---	<10	<10	<10	<10
Floating Biphenyl	mg/L	309	127 ^b	144	51 ^b	214
pH	---	---	13.8	13.8	13.8	13.8
Biphenyl ^c	mg/L	309	1.1	---	0.71	---
Benzene ^c	mg/L	27.5	1.1	---	0.53	---
TOC	mg/L	8,951 (excludes antifoam)	< 10	---	< 10	---
TIC	mg/L	2,739	6,780	---	7,270	---

^a Soluble biphenyl is biphenyl dissolved in the aqueous phase.

^b The floating biphenyl was not physically removed initially. Hence, values may have skewed to the low side.

^c This is from SVOC/VOC analysis of the treated slurry.

TPB destruction > 99.99%. TPB daughter compounds (3PB, 2PB, 1PB), and phenol are destroyed to below detection limits.

Confirmation Tests – Treated Simulant Data

	Units	Diluted Feed Slurry Conc. (Calculated)	Test 16A	Test 16B	Test 16C	Test 16D
Formate	mg/L	None	< 10	---	< 10	---
Oxalate	mg/L	None	< 10	---	< 10	---
Acetate	mg/L	None	< 100	---	< 100	---
Acetic Acid	mg/L	None	---	<153	---	---
Acrylic Acid	mg/L	None	---	<2.50	---	---
Butyric Acid	mg/L	None	---	<130	---	---
Formic Acid	mg/L	None	---	<97.0	---	---
Fumaric Acid	mg/L	None	---	<1.00	---	---
Isobutyric Acid	mg/L	None	---	<104	---	---
Maleic Acid	mg/L	None	---	<2.00	---	---
Malonic Acid	mg/L	None	---	<153	---	---
Propionic Acid	mg/L	None	---	<103	---	---
Succinic Acid	mg/L	None	---	<175	---	---
Oxalic Acid	mg/L	None	---	<14	---	---
Glyoxalic Acid	mg/L	None	---	<176	---	---

All the organic acids were below detection limits. Typically, WAO does not destroy the low molecular weight carboxylic acids. Cu catalyst may have aided in their destruction.

Confirmation Tests – Treated Simulant Data

	Units	Diluted Feed Slurry Conc. (Calculated)	Test 16A	Test 16B	Test 16C	Test 16D
Free OH ⁻	mg/L	1.799 M (includes 2M NaOH as diluent)	0.229	---	0.271	---
Carbonate	mg/L	13,681	33,874	---	36,322	---
Nitrite	mg/L	10,469	6,310	---	6,300	---
Nitrate	mg/L	6,541	10,600	---	10,800	---
Phosphate	mg/L	252	158	---	146	---
Sulfate	mg/L	889 (includes catalyst)	1,080	---	1,050	---
Chloride	mg/L	111	143	---	103	---
Fluoride	mg/L	8.7	< 2	---	< 2	---
Insoluble Solids	wt %	1.01	0.01	---	0.01	---
B	mg/L	311	262	---	270	---
K	mg/L	1,260	1,227	---	1,327	---

Residual solids data indicate virtually all TPB is destroyed.

Confirmation Tests – Off-Gas Data

	Units	Test 16A	Test 16B	Test 16C	Test 16D
Off-Gas Volume	L	12.8	11.0	13.6	12.4
Off-Gas Temp.	°C	18.3	17.3	21.2	25.2
CO ₂	vol%	<0.5	<0.5	<0.5	<0.5
O ₂	vol%	7.9	6.5	9.0	7.8
N ₂	vol%	90.6	92.1	89.8	91.6
CO	vol%	<0.1	<0.1	<0.1	<0.1
THC (as ethane - C ₂ H ₆)	ppmv	1,460	1,612	1,140	1,180
Methane (CH ₄)	ppmv	<50	<50	<50	<50
Hydrogen	vol%	0.054	<0.05	0.052	<0.05
Benzene (C ₆ H ₆)	ppmv	347	1,243	---	---
Benzene (as ethane - C ₂ H ₆)	ppmv	902	3,232	---	---
O ₂ Uptake	g/L*	32.0	34.4	29.2	32.5

* This is the mass of oxygen consumed by the oxidation of constituents in the slurry. The units are grams of oxygen per liter of slurry treated in the autoclave.

Even though > 50% of off-gas is benzene, it is << benzene LFL (0.06X – 0.25X LFL)

MOC Tests

➤ MOC Coupons

- Nickel 201
- Inconel 690
- Inconel 600
- Monel K-500
- 316-L Stainless Steel
- 304-L Stainless Steel
- 2205 Duplex Stainless Steel

Results indicate the first four on the list are potentially acceptable

➤ Coupons evaluated using ASTM corrosion methods

Summary/Path Forward

- Bench-scale testing results indicate WAO is effective in destroying TPB and byproducts
- Continuous-flow pilot-scale testing is needed
 - Optimize the identified bench-scale conditions
 - A better measure of the biphenyl destruction
 - More realistic off-gas data
 - Demonstrate robust, continuous, and safe steady-state operations
 - Identify and resolve any pertinent issues that may emerge
 - Biphenyl destruction and its residual levels in treated slurry and off-gas
 - Benzene/other flammable compounds generation and their residual levels in treated slurry and off-gas
 - Solids/scale formation
 - Pumpability of feed slurry
 - Efficacy of depressurization system
- A 1000-hour MOC test is required to confirm MOC findings

Acknowledgments

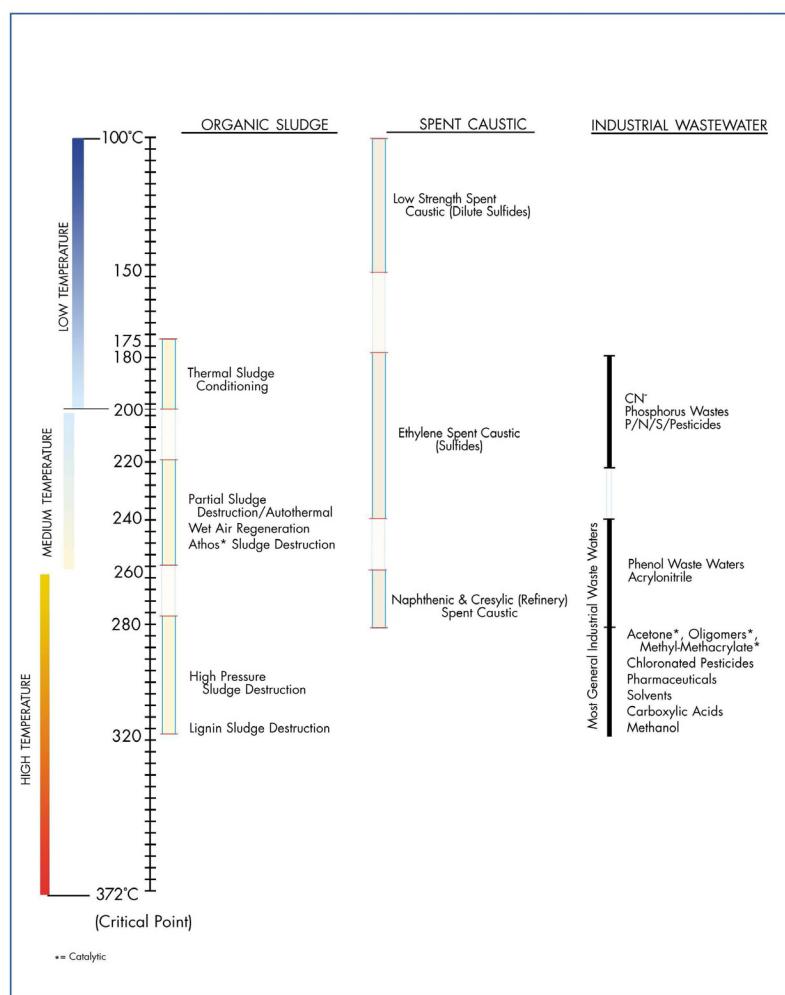
- The work was conducted at the facilities of Siemens Water Technologies Corporation in Rothschild, Wisconsin
 - Richard W. Lehmann, Project Manager
 - Bryan Kumfer, Oxidation Chemist
 - Enviroscan personnel
- Savannah River National Laboratory
 - Kim Wyszynski
 - Tom White and Analytical Development personnel
 - David Best

Backup Slides

History of WAO Commercialization

- First patented in Sweden in 1911 for destruction of spent pulping liquors.
- 1930s and 1940s
 - First commercialized as the Zimmermann Process for the manufacture of artificial vanilla flavoring (vanillin). Vanillin was produced by the low temperature (160°C) WAO of the lignosulfonic acids in spent pulping liquor from paper mills.
- 1950s
 - High temperature/pressure WAO was commercialized for the destruction of paper mill waste liquor and sludge
- Early 1960s
 - Low temperature/pressure WAO was applied to biological sludges, to enhance dewaterability.
 - Called thermal sludge conditioning (TSC) or Low Pressure Oxidation (LPO).
- Late 1960s and Early 1970s
 - WAO was used to regenerate the spent powdered activated carbon for reuse in the PACT® system.
 - Referred to as wet air regeneration (WAR).
- 1970s to Present
 - Commercialized for the treatment of industrial wastewaters including catalytic and non-catalytic WAO.

WAO APPLICATION SPECTRUM



WAO APPLICATIONS

- Petroleum refinery spent caustic
 - High pH
 - Contains sulfidic, naphthenic, cresylic, and phenolic compounds.
 - 240 - 260°C
 - ~3 gpm flow rate
- Petroleum Refinery Spent Caustic WAO Unit - Rio de Janeiro, Brazil



Zimpro® WAO System

WAO APPLICATIONS

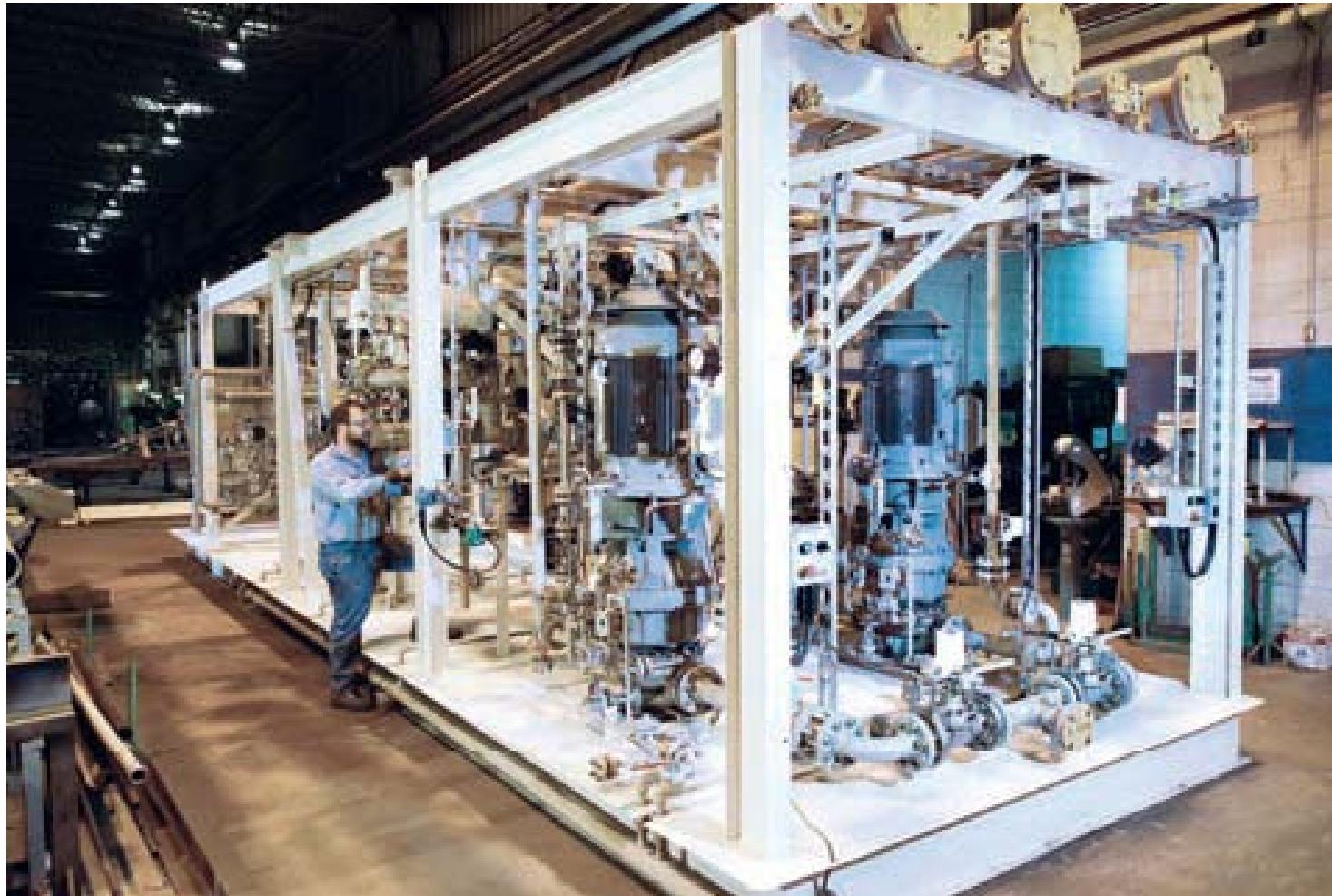
- Design conditions of Rio de Janeiro Refinery Spent Caustic WAO Unit.
- Refinery Spent Caustic WAO Performance (Temp = 246 °C)

Feed Rate	0.88 gpm
Dilution Feed Water	1.76 gpm
Reactor Temperature	260°C
Reactor Pressure	86 atm

	Reactor Inlet	Reactor Effluent
COD (mg/L)	72,000	15,000
COD reduction	--	79.2%
Phenols (mg/L)	1,700	3
Sulfide - S (mg/L)	2,700	<1
Mercaptans - CH ₃ SH (mg/L)	2,800	2
Thiosulfate - S ₂ O ₃ (mg/L)	640	<26
pH	13.43	8.24

Zimpro® WAO System

Zimpro® WAO Skid (shipping layout)



Zimpro® WAO Skid on a Truck

